Sulfur isotopes in sediment-hosted orogenic gold deposits: Evidence for an early timing and a seawater sulfur source

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ABSTRACT

We report sulfur isotopic compositions of sulfides of various paragenetic stages in the giant Sukhoi Log sediment-hosted orogenic Au deposit in Russia. The overall mean value and the significant variability in early pyrite indicate that the sulfur was from the reduction of seawater sulfate. The later generations of sulfide have $\delta^{34}S$ values in successively smaller ranges, coincident with the mode that is around the median value of the whole data set. Together with textural evidence, sulfide trace element data, and gold occurrence, the data demonstrate that metamorphism has gradually homogenized the early sulfur, accompanied by the segregation of quartz and the release of Au from the lattice of early pyrite and its reprecipitation as inclusions in later pyrite. The S isotopic compositions of sulfides in Sukhoi Log, and many other major orogenic Au deposits hosted in sedimentary rocks of various ages, show a pattern generally parallel to the seawater sulfate curve through geologic time, indicating that the sulfur in most sediment-hosted orogenic Au deposits was probably also originally from the reduction of seawater sulfate. We conclude that sulfidation and gold mineralization in many sediment-hosted orogenic gold deposits was early during basin evolution when seawater was the principal active fluid, rather than later, during or after basin inversion, as proposed in current models.

INTRODUCTION

Because gold is believed to be mostly transported as bisulfide complexes in orogenic deposits (e.g., Groves et al., 2003; Goldfarb et al., 2005), the source of the sulfur is important to the understanding of the source of Au, the source of the hydrothermal fluids, and the genesis of the deposits. However, the S source of such deposits has been equivocal for many decades. Various hypotheses have been proposed, for example, S introduced by metamorphic fluids from wall rock (e.g., Sangster, 1992; Goldfarb et al., 1997) or from deep crust at amphibolite or granulite facies (e.g., Kerrich and Fryer, 1979; Phillips et al., 1987), S from the mantle depths (e.g., Perring et al., 1987; Barley and Groves, 1990), and S from magmas (e.g., Burrows and Spooner, 1985).

In this paper we present S isotope data from the giant Sukhoi Log orogenic gold deposit, Russia (1100 t Au averaging 2.45 g/t; Distler et al., 2004), and discuss the genesis. Then, by comparing the S isotope pattern of Sukhoi Log with other sediment-hosted orogenic gold deposits in relation to the secular seawater sulfate S isotope curve, we argue that the S from other deposits was probably also from the reduction of seawater sulfate. This conclusion has major implications for the genesis of sediment-hosted orogenic deposits.

SUKHOI LOG GOLD DEPOSIT

Sukhoi Log is within the Patom Highlands orogen (Fig. 1), a Neoproterozoic passive margin sequence that accumulated on the eastern margin of the Siberian craton and was subsequently deformed and metamorphosed at 516 ± 22 Ma (Laverov et al., 2000). The sequence also contains sedimentary exhalative (SEDEX) style base metal deposits, including the Kholodninskoe Pb-Zn deposit (Fig. 1; Distanov et al., 1982). The host rock is an organic-bearing pyritic black shale and siltstone sequence with a maximum sedimentation age of 600 Ma (Meffre et al., 2008). The mineralization occurs in the core of a tight overturned anticline. It consists of discontinuous bedding-parallel quartz-sulfide (dominantly pyrite) segregations and veins, disseminated bedding-parallel pyrite, and minor pyrite nodules, coarse euhedral pyrite, and cross-cutting quartz veins. The mineralized zone forms a shallow-dipping tabular body parallel to the axial plane cleavage, with a high-grade gold zone (>4 g/t) concentrated within the general hinge zone of the fold, where folded quartz-pyrite veinlets are more intensely developed (Distler et al., 2004). The best gold grades are associated with the narrow bedding-parallel quartz-pyrite segregations and veins that have been folded by the main deformation event. No sulfate minerals have been found or reported.

Detailed paragenetic studies of the mineralization and host rocks by Large et al. (2007) defined six stages of pyrite (py) development, including syngenetic framboidal or fine-grained py1, early diagenetic py2, late diagenetic to early metamorphic py3, synmetamorphic to late metamorphic py4, late metamorphic py5, and late-stage py6 (Fig. 2). Typically py4 grains have narrow quartz pressure shadows and there is little py1 in their immediate vicinity. In fold hinge zones there are quartz-pyrite segregations and irregular, discontinuous veins that have been interpreted as coalesced segregations. Pyrite in such segregations and veins (vein pyrite) is typically zoned from core to rim as arsenopyrite → py3 → py4 → py5 (Fig. 2F). Pyrrhotite, chalcopyrite, sphalerite, and arsenopyrite first appear as inclusions in py3, and minor pyrrhotite and arsenopyrite are also associated with py4 and py5.

Large et al. (2007) reported laser ablation–inductively coupled plasma–mass spectrometry analyses of the various pyrite types. The synsedimentary py1 contains the highest levels of lattice-bound Au and As and a suite of trace elements (Mo, Sb, Ni, Co, Se, Te, Ag, Cu, Pb, Zn, Mn, Ba, Cr, U, V) that are similar to those concentrated by organic processes in euxinic sedimentary environments. Later generations of pyrite, from py2 to py5, including vein pyrite, contain progressively lower contents of lattice-bound Au and most other trace elements, but significant inclusions of free gold and gold telluride (Large et al., 2007). Monazite geochronology and Pb-Pb dating of pyrite indicate that the formation of pyrite and introduction and/or remobilization of gold was a multistage process, from sedimentation and/or diagenesis through deformation and metamorphism (Meffre et al., 2008).

SUKHOI LOG S ISOTOPES

Sulfur isotopes were measured using both conventional (±0.3‰, 2σ; Robinson and Kasakabe, 1975) and laser ablation methods (±1.0‰, 2σ; Huston et al., 1995); the results are presented in Figure 3. The 35 analyses of py1 and py2 range from –6.5‰ to +19.3‰, with a median of 10.6‰, and 50% of the data are in a range from 3.4‰ to 12.1‰ (1st and 3rd quartile). Spatially the S isotope compositions of py1 vary greatly over a short distance, e.g., 8.7‰ over 7 cm (Fig. 2A). The 26 analyses of py3 are from –2.7‰ to +16.7‰, with a median of 11.5‰, and 50% of the data are in a range from 7.7‰ to 13.0‰. The range for the 55 py4 analyses is 4.3‰–24.0‰, the median 10.9‰, and 50% of the data range from 9.7‰ to 13.5‰. Although the total range of the py4 $\delta^{34}S$ values is only slightly smaller than the earlier pyrites, the spatial variation of S isotopes is much smaller. For example, py4 crystals 9 cm apart have almost identical S isotope compositions (Fig. 2E), and large variations occur only over large distances (>~15 m). We analyzed py5 by the laser ablation method; the range of the 25 measurements

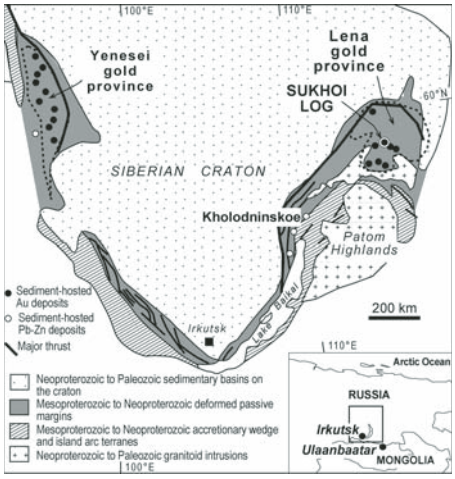

Figure 1. Location of Sukhoi Log deposit (after Large et al., 2007).

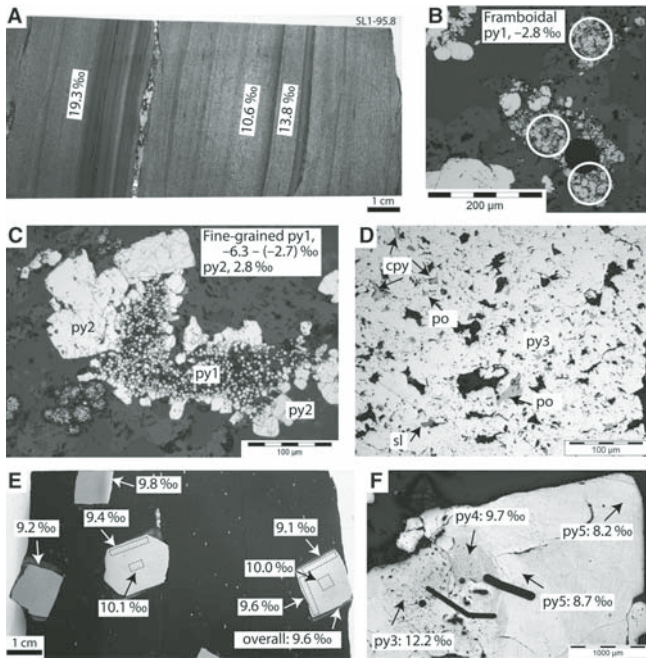

Figure 2. Textural features of different types of pyrite and their S isotope compositions. Abbreviations: py—pyrite; cpy—chalcopyrite; po—pyrrhotite; sl—sphalerite. A: Bedding-parallel py1, with large variation over short distance. B: Framboidal pyrite, typically with the lightest S isotope compositions. C: Fine-grained pyrite in the same band as framboidal pyrite also has low $\delta^{34}S$ values; py2 recrystallized and/or overgrown from py1 also has low $\delta^{34}S$ values. D: py3 typically contains inclusions of po, cpy, sl, native Au, and silicates. E: py4 has little variation within individual grain, and intergranular variation over 7 cm is minimal. F: Pyrite in quartz-pyrite segregation or veins is mostly py5 and may contain py3 and/or py4, and native Au. The $\delta^{34}S$ values of py5 have a smaller range (~7‰ to 13‰), coincident with the mode and central part of whole sulfide $\delta^{34}S$ range.

is much smaller, 7.1‰–12.6‰. The conventional analyses of drilled powders of vein pyrite, mostly py5, but likely containing py3 and/or py4, yielded a similarly small range but with slightly higher $\delta^{34}S$ values, 11.1‰–16.9‰. The S isotope compositions of pyrrhotite (12 analyses) and arsenopyrite (2 analyses) are also concentrated in the 7‰–13‰ range. No correlation between S isotope compositions and stratigraphy or lithology was found. Overall, the 183 S isotope analyses have a large variation, from –6.5‰ to +24.0‰, with the majority in the range of 7‰–17‰, and a median of 10.4‰ (Fig. 3).

COMPARISON WITH OTHER SEDIMENT-HOSTED OROGENIC GOLD DEPOSITS

Sulfur isotope data from Sukhoi Log and 15 other sediment-hosted gold deposits were plotted in Figure 4. The other deposits were selected to cover a large age span. Deposits hosted in volcanic or intrusive rocks were not included in this compilation. The S isotope data were plotted against the sedimentation age of the host rocks, together with the $\delta^{34}S$ seawater sulfate curve (Claypool et al., 1980; Strauss, 2004). The statistics of the data are summarized in GSA Data Repository Table DR1[1].

Figure 4 shows that the variation in S isotope compositions of the deposits through geologic time has a pattern similar to the seawater sulfate curve. The $\delta^{34}S$ values of the sulfides are typically ~15‰–20‰ lighter than the coeval seawater sulfate, though the difference can be smaller (~10‰) or larger (~30‰).

DISCUSSION AND CONCLUSIONS

Source of Sulfur in the Sukhoi Log Deposit

The S isotope compositions of early sulfides (syngenetic and diagenetic: py1 and py2) in the Sukhoi Log deposit have large variations, in terms of both total range (~26‰) and stratigraphic variation (e.g., ~9‰ change over 7 cm). Such large variations preclude the possibility that the S is from either a magmatic source (Ohmoto, 1986), or a homogenized deep metamorphic source (e.g., Groves et al., 2003). Instead, the S isotope data indicate that the S is sourced from seawater sulfate during sedimentation and diagenesis, consistent with the textural evidence of a syngenetic origin (Large et al., 2007). This interpretation is further supported by the similarity in $\delta^{34}S$ ranges and medians of the data sets at Sukhoi Log (–6.5‰ to

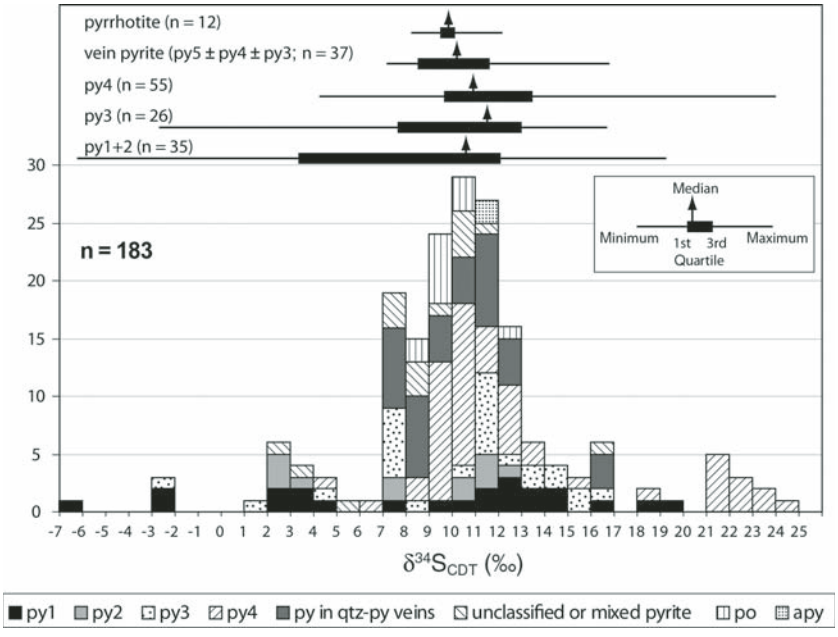

Figure 3. Histogram and statistics of S isotope data of sulfides from Sukhoi Log deposit. Abbreviations: py—pyrite; po—pyrrhotite; qtz—quartz; apy—arsenopyrite; CDT—Vienna Canyon Diablo Troilite.

[1]GSA Data Repository item 2008242, Table DR1, summary of S isotopes of sediment-hosted Au deposits, is available online at www.geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

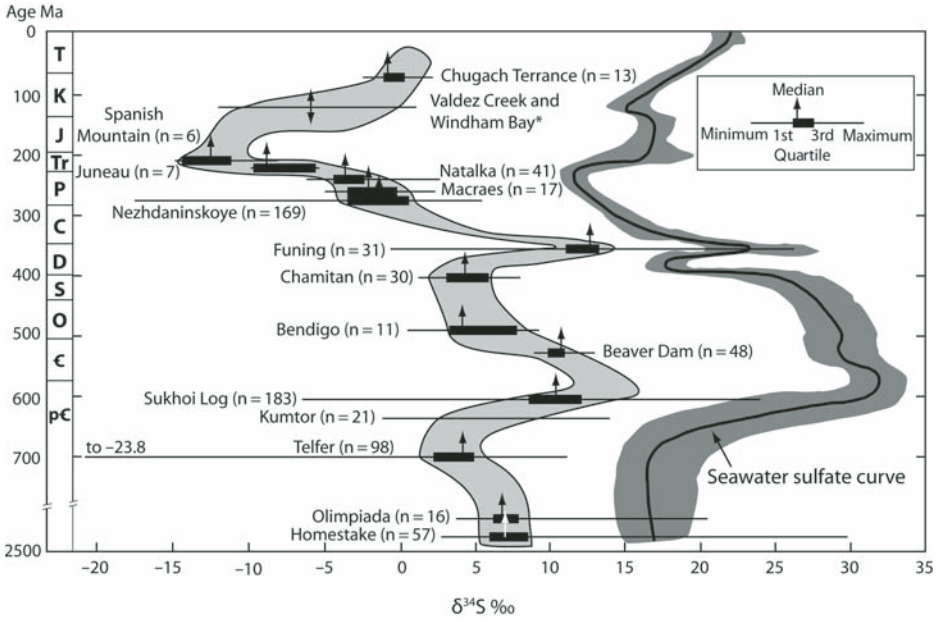

Figure 4. Variation of sulfide S isotopic compositions in sediment-hosted orogenic gold deposits through geologic time and seawater sulfate curve.

+24.0‰, median 10.4‰) and at the nearby, and age equivalent, Kholodniskoe SEDEX Zn-Pb-Ag deposit (range –9.5‰ to +25.4‰, median 9.5‰; n = 269: Distanov et al., 1988). Typically, S in SEDEX deposits is interpreted to be from seawater (e.g., Goodfellow et al., 1993).

The seawater sulfate could have been reduced by several processes, or a combination of them. Bacterial sulfate reduction can explain the large variations (e.g., Ohmoto, 1986); experiments have shown that biogenic sulfides can have $\delta^{34}S$ values 2‰–46‰ lighter than the seawater sulfate (Detmers et al., 2001, and references therein). Abiotic thermochemical reduction of sulfate can cause a fractionation of 10‰–25‰ (Harrison and Thode, 1957; Seal, 2006, and references therein). At Sukhoi Log, the framboidal texture of some pyrite may indicate a bacterial origin, whereas the presence of an abnormal amount of Au-bearing syngenetic pyrite may be the result of synsedimentary hydrothermal activity, as proposed by Large et al. (2007). Therefore it is possible that both bacterial reduction and abiotic reduction related to synsedimentary hydrothermal activity have played a role in fixing the S, Au, and As into the sediments as gold-bearing arsenian pyrite.

Homogenization of Sulfur Related to Metamorphism and Au Concentration

From early synsedimentary to late metamorphic, the different generations of pyrite at Sukhoi Log have successively narrower ranges of $\delta^{34}S$ values, whereas the median values stay similar (Fig. 3). Although the overall ranges for py3 and py4 are only slightly narrower than those of py1 and py2, the spatial variation is much smaller and the 1st to 3rd quartile ranges narrower. The latest metamorphic pyrite (py5) and pyrrhotite have $\delta^{34}S$ values in a small range (7.1‰–12.6‰, 8.2‰–12.2‰), concentrating around the median value of the whole data set (10.4‰). Their total ranges are similar to the mode of all sulfide data at Sukhoi Log (7‰–13‰; Fig. 3). We interpret this trend as the result of gradual homogenization of S during metamorphism.

The increasing effect of metamorphism on py1 to py5 was demonstrated by Large et al. (2007) to also coincide with the evolution of Au occurrence from purely lattice-bound Au in synsedimentary pyrite (py1) to totally free Au as inclusions in py5 and quartz-pyrite segregations. This indicates that the homogenization of S isotopes is accompanied by the remobilization and concentration of Au. In fact, py5, the only pyrite type that exhibits significant S isotope homogenization at the deposit scale, is mostly hosted in quartz-sulfide segregations and veinlets that bear the highest Au grades (as free gold) in the deposit.

In summary, sulfur, arsenic and gold were introduced into the sedimentary rock as syngenetic and diagenetic gold-bearing arsenian pyrite, with the sulfur produced by a mixture of both hydrothermal reduction and bacterial reduction of seawater sulfate. The original S in pyrite was gradually homogenized during metamorphism, together with the release of invisible gold and other elements from the early syngenetic and diagenetic pyrite, resulting in the formation of free gold in the later metamorphic pyrite. Significant S isotope homogenization only occurred late in the history of the deposit during maximum deformation and folding, when py5 overgrew the earlier pyrite stages and quartz segregations developed in pressure shadows.

Sulfur Source of Sediment-Hosted Orogenic Au Deposits and its Implications

The fact that the S isotope compositions of many orogenic sediment-hosted deposits vary in a parallel fashion to the seawater sulfate curve (Fig. 4) indicates that the sulfur in the deposits was derived by reduction of seawater sulfate. A similar pattern has previously been reported for volcanic-hosted massive sulfide (VHMS) and SEDEX Zn-Pb-Cu deposits (Sangster, 1968; Large, 1992; Goodfellow et al., 1993; Huston, 1999), and remains one of the strongest arguments that the S in these deposits is principally reduced seawater sulfate rather than magmatic or metamorphic sulfur. The sulfide $\delta^{34}S$ values in most sediment-hosted gold deposits have a mode consistently ~15‰–20‰ lighter than the coeval sulfates (Fig. 4), again similar to base metal SEDEX and VHMS deposits, indicating that at least part of the reduction was abiotic and hydrothermal ($\Delta^{34}S_{sulfate\text{-}sulfide}$ = 10‰–25‰; Harrison and Thode, 1957), especially in deposits hosted in Phanerozoic sediments. If there were no hydrothermal reduction, the sulfate-sulfide S isotope fractionation would be >40‰, commonly ~60‰, in Phanerozoic sedimentary rocks (Strauss, 1997). Such a large fractionation is believed to be caused by initial bacterial sulfate reduction ($\Delta^{34}S_{sulfate\text{-}sulfide}$ = 2‰–46‰; e.g., Habicht and Canfield, 1997) and subsequent disproportionation reactions ($\Delta^{34}S_{sulfate\text{-}sulfide}$ = 7‰–20‰; e.g., Bottcher et al., 2001). On the other hand, the large $\delta^{34}S$ variations present in some sediment-hosted gold deposits were probably caused by bacterial reduction in addition to the hydrothermal reduction. Goldfarb et al. (1997) also noticed that $\delta^{34}S$ of sulfides in orogenic Au deposits in Alaska has a temporal variation pattern similar to that of seawater sulfate, on the basis of which they proposed that the S source reservoir of the Alaska deposits was the ore-hosting sediments. Our study argues further that the S in similar sediment-hosted deposits worldwide is ultimately from seawater, with S and Au both deposited during sea-floor hydrothermal activity. The later homogenization of S and concentration of Au during metamorphism are supported by sulfide textures and trace element characteristics.

There is general consensus that Au deposition in orogenic gold deposits is by a process of sulfidation of preexisting Fe minerals such as Fe carbonates, magnetite, or Fe silicates (e.g., Phillips and Groves, 1984; Groves et al., 2003; Goldfarb et al., 2005). This implies that the Au and S are transported together in the ore fluid, and added to the rock during the ore-forming process. The relationship between S isotopes in gold-ore pyrite and the seawater sulfate curve through

time revealed here is compelling evidence that the ore fluid for Sukhoi Log and most other sediment-hosted orogenic deposits contained a major proportion of seawater S. The sulfidation process responsible for gold mineralization was thus a very early event during the basin history, when contemporaneous seawater was an active crustal fluid. This result is contrary to current theories on orogenic gold deposits that require a very late timing for the sulfidation and gold mineralization process, usually during deformation and metamorphism or sometimes after metamorphism (e.g., Groves et al., 2000; Hagemann and Cassidy, 2000). We still consider the role of metamorphism to be important in producing economic deposits, due to the associated recrystallization of early syngenetic and diagenetic gold-bearing pyrite, which release invisible gold as free gold, to become upgraded and coarsened in grain size in structural sites such as anticlines and shear zones.

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REFERENCES CITED

Barley, M.E., and Groves, D.I., 1990, Deciphering the tectonic evolution of Archaean greenstone belts; the importance of contrasting histories to the distribution of mineralization in the Yilgarn Craton, Western Australia: Precambrian Research, v. 46, p. 3–20, doi: 10.1016/0301-9268(90)90064-W.

Bottcher, M.E., Thandrup, B., and Vennemann, T.W., 2001, Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur: Geochimica et Cosmochimica Acta, v. 65, p. 1601–1609, doi: 10.1016/S0016-7037(00)00628-1.

Burrows, D.R., and Spooner, E.T.C., 1985, Generation of an Archaean H_2O-CO_2 fluid enriched in Au, W & Mo by fractional crystallization in the Mink Lake intrusion, NW Ontario: Geological Society of America Abstracts with Programs, v. 17, p. 536.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen in marine sulfate and their initial interpretation: Chemical Geology, v. 28, p. 199–206, doi: 10.1016/0009-2541(80)90047-9.

Detmers, J., Brüchert, V., Habicht, K.S., and Kuever, J., 2001, Diversity of sulfur isotope fractionations by sulfate-reducing prokaryotes: Applied and Environmental Microbiology, v. 67, p. 888–894, doi: 10.1128/AEM.67.2.888-894.2001.

Distanov, E.G., Kovalev, K.R., Tarasova, R.S., Kochetkova, K.V., Ponomarev, V.G., Buslenko, A.I., Gas'kov, I.V., and Kuznetsov, V.A., 1982, The pyrite-polymetallic deposit of the Precambrian of Kholodnina and Baikal region: Trudy Instituta Geologii i Geofiziki (Novosibirsk), v. 526, 207 p.

Distanov, E.G., Gas'kov, I.V., Grinenko, L.N., and Pertseva, A.P., 1988, Sulfur isotope composition of ore and rocks of the Kholodninskii pyrite-polymetal deposit: Soviet Geology and Geophysics, v. 29, no. 7, p. 55–62.

Distler, V.V., Yudovskaya, M.A., Mitrofanov, G.L., Prokof'ev, V.Y., and Lishnevskiy, E.N., 2004, Geology, composition and genesis of the Sukhoi Log noble metals deposit, Russia: Ore Geology Reviews, v. 24, p. 7–44, doi: 10.1016/j.oregeorev.2003.08.007.

Goldfarb, R.J., Miller, L.D., Leach, D.L., and Snee, L.W., 1997, Gold deposits in metamorphic rocks of Alaska, *in* Goldfarb, R.J., and Miller, L.D., eds., Mineral deposits of Alaska: Economic Geology Monograph 9, p. 151–190.

Goldfarb, R.J., Baker, T., Dube, B., Groves, D.I., Hart, C.J.R., and Gosselin, R., 2005, Distribution, character, and genesis of gold deposits in metamorphic terranes, *in* Hedenquist, J.W., et al., eds., Economic Geology 100th Anniversary Volume: Littleton, Colorado, Society of Economic Geologists, p. 407–450.

Goodfellow, W.D., Lydon, J.W., and Turner, R.J.W., 1993, Geology and genesis of stratiform sediment-hosted (SEDEX) zinc-lead-silver sulphide deposits, *in* Kirkham, R.V., et al., eds., Mineral deposit modeling: Geological Association of Canada Special Paper 40, p. 201–251.

Groves, D.I., Goldfarb, R.J., Knox-Robinson, C.M., Ojala, J., Cardoll, S., Yun, G., and Holyland, P., 2000, Late-kinematic timing of orogenic gold deposits and its significance for computer-based exploration techniques with emphasis on the Yilgarn block, Western Australia: Ore Geology Reviews, v. 17, p. 1–38, doi: 10.1016/S0169-1368(00)00002-0.

Groves, D.I., Goldfarb, R.J., Robert, F., and Hart, C.J.R., 2003, Gold deposits in metamorphic belts: Overview of current understanding, outstanding problems, future research, and exploration significance: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 98, p. 1–29.

Habicht, K.S., and Canfield, D.E., 1997, Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments: Geochimica et Cosmochimica Acta, v. 61, p. 5351–5361, doi: 10.1016/S0016-7037(97)00311-6.

Hagemann, S.G., and Cassidy, K.F., 2000, Archean orogenic lode gold deposits: Reviews in Economic Geology, v. 13, p. 9–68.

Harrison, A.G., and Thode, H.G., 1957, The kinetic isotope effect in the chemical reduction of sulphate: Faraday Society Transactions, v. 53, p. 1648–1651, doi: 10.1039/tf9575301648.

Huston, D.L., 1999, Stable isotopes and their significance for understanding the genesis of volcanic-hosted massive sulfide deposits; a review: Reviews in Economic Geology, v. 8, p. 157–179.

Huston, D.L., Power, M., Gemmell, J.B., and Large, R.R., 1995, Design, calibration and geological application of the first operational Australian laser ablation sulfur isotope microprobe: Australian Journal of Earth Sciences, v. 42, p. 549–555, doi: 10.1080/08120099508728224.

Kerrich, R., and Fryer, B.J., 1979, Archaean precious-metal hydrothermal systems, Dome Mine, Abitibi greenstone belt; II, REE and oxygen isotope relations: Canadian Journal of Earth Sciences, v. 16, p. 440–458.

Large, R.R., 1992, Australian volcanic-hosted massive sulfide deposits; features, styles, and genetic models: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 87, p. 471–510.

Large, R.R., Maslennikov, V.V., Robert, F., Danyushevsky, L.V., Scott, R.J., and Chang, Z., 2007, Multi-stage sedimentary and metamorphic origin of pyrite and gold in the giant Sukhoi Log deposit, Lena Goldfield, Russia: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 102, p. 1233–1267.

Laverov, N.P., Prokof'ev, V.Y., Distler, V.V., Yudovskaya, M.A., Spiridonov, A.M., Grebenshchikova, V.I., and Matel, N.L., 2000, New data on conditions of ore deposition and composition of ore forming fluids in the Sukhoi Log gold-platinum deposit: Doklady Earth Sciences, v. 371, p. 357–361.

Meffre, S., Large, R.R., Scott, R., Woodhead, J., Chang, Z., Gilbert, S.E., Danyushevsky, L.V., Maslennikov, V., and Hergt, J.M., 2008, Age and pyrite Pb-isotopic composition of the giant Sukhoi Log sediment-hosted gold deposit, Russia: Geochimica et Cosmochimica Acta, v. 72, p. 2377–2391, doi: 10.1016/j.gca.2008.03.005.

Ohmoto, H., 1986, Stable isotope geochemistry of ore deposits: Reviews in Mineralogy, v. 16, p. 491–559.

Perring, C.S., Groves, D.I., and Ho, S.E., 1987, Constraints on the source of auriferous fluids for Archaean gold deposits, *in* Ho, S.E., and Groves, D.I., eds., Advances in understanding Precambrian gold deposits: Geology Department and University Extension, University of Western Australia, Publication 11, p. 287–306.

Phillips, G.N., and Groves, D.I., 1984, Fluid access and fluid-wallrock interaction in the genesis of the Archean gold-quartz vein deposit at Hunt mine, Western Australia, *in* Foster, R.P., ed., Gold '82: The geology, geochemistry, and genesis of gold deposits: Rotterdam, A.A. Balkema, p. 389–416.

Phillips, G.N., Groves, D.I., and Brown, I.J., 1987, Source requirements for the Golden Mile, Kalgoolie: Significance to the metamorphic replacement model for Archean gold deposits: Canadian Journal of Earth Sciences, v. 24, p. 1643–1651.

Robinson, B.W., and Kasakabe, M., 1975, Quantitative preparation of sulfur dioxide for $^{34}S/^{32}S$ analyses from sulphides by combustion with cuprous oxide: Analytical Chemistry, v. 47, p. 1179–1181, doi: 10.1021/ac60357a026.

Sangster, D.F., 1968, Relative sulfur isotope abundances of ancient seas and stratabound sulphide deposits: Geological Association of Canada Proceedings, v. 17, p. 79–91.

Sangster, A.L., 1992, Light stable isotope evidence for a metamorphogenic orogen for bedding-parallel, gold-bearing veins in Cambrian flysch, Meguma Group, Nova Scotia: Exploration and Mining Geology, v. 1, p. 69–79.

Seal, R.R., II, 2006, Sulfur isotope geochemistry of sulfide minerals: Reviews in Mineralogy and Geochemistry, v. 61, p. 633–677, doi: 10.2138/rmg.2006.61.12.

Strauss, H., 1997, The isotopic composition of sedimentary sulfur through time: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 132, p. 97–118, doi: 10.1016/S0031-0182(97)00067-9.

Strauss, H., 2004, 4 Ga of seawater evolution: Evidence from the sulfur isotopic composition of sulfate, *in* Amend, J.P., et al., eds., Sulfur biogeochemistry—Past and present: Geological Society of America Special Paper 379, p. 195–205.

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